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Should Ground Water Samples from Monitoring Wells Be Filtered Before Laboratory Analysis?

This is the third of four "Point-Counterpoint" articles planned to appear in this column. These articles are based on discussion sessions held at the Sixth National Aquifer Restoration and Ground Water Monitoring Conference. A oriest article outlining each speaker's opinion is offered first, followed by the transcript of the discussion session during which attendees have a chance to ask the speakers questions on the subject.

Opinion I

by Olin C. Braids, Ph.D.

The issue of filtration of ground water samples is integral to discussions of proper protocol in ground reampling. There are those who believe that filtration to the preparation of a water sample in order to get a lep. In taking and accurate analysis. There are others who are also ye convinced that filtration will deletenously affect the water sample and lead to difficulties with the data acquired from it.

Each side of this issue has merit because the reasons for the ground water analysis vary and the objectives in the analytical program also differ. There are legitimate situations in which a ground water sample should not be futered before it is analyzed for its chemical constituents in the laboratory and there are circumstances dictating that an accurate analysis is only obtained when filtration is accomplished. This discussion will address the situations in which filtration should be included in sample preparation.

Filtration in this context is filtration through a 0.45 µm pore-size membrane. The same principles also apply if the filtration medium is glass fiber or paper. Frequently, practical limitations of time and sample characteristics dictate the use of glass fiber or paper as prefilters before the final membrane step.

In dealing with the subject of filtration, one must address the water quality parameters that could be affected either by the act of filtration or by the failure to filter. The following characteristics of water are those that would be affected by filtration or the lack thereof.

The partial pressure of dissolved gases in water withdrawn from the aquifer could be affected by the process of filtration. The relationship of oxygen, carbon dioxide, and perhaps other trace gases influences the pH and the oxidation-reduction potential of the water. In cases where the partial pressure of a gas such as carbon dioxide is significantly affected by the added input from decomposition or some other process, the chemical characteristics of water can change when that relationship is disrupted.

The standard protocol of long standing for dissolved metals is to perform a filtration. Any suspended matter occurring in water is likely to have metal ions adsorbed on it. If the water is preserved with acid prior to analysis as the standard protocols call for, the metals are likely to be desorbed from the solids. This would result in dissolved concentrations of metals being higher than onginally existed.

Iron is frequently found as a constituent of ground water in concentrations, which result in its precipitation when the water is exposed to the oxygen of the atmosphere. Under these conditions the sample of ground water should be filtered as rapidly as possible to prevent contact with the air and to remove any suspended material prior to the addition of acidic preservatives. If the sample contains suspended matter and dissolved iron, addition of the acid prior to filtration may desorb metals. from the suspended matter. If the sample is allowed to be in contact with air for even a matter of minutes prior to filtration, the iron may precipitate and co-precipitate or adsorb metals that were in solution. Acidification of the sample at this point may redissolve the fron but may also bring into solution more of the other metals than were in solution at the time the sample was collected.

The presence of suspender, matter in water, where the water has been in contact with or is contaminated with very slightly soluble organic compounds poses a problem similar to rharofiche metals. Slightly soluble compounds such to PC fis, polynuclear aromatic hydrocarbonic photocarbonic and infiltered sample is extracted with organic solvent malyzed, the compounds will desorb and appear as a long were in solution.

Radioactive gases such as radon could be affected by filtration because of the pressure change across the filtra-

tion medium. There are methods to be discussed later that can eliminate or minimize losses of gases or voiatile compounds in water during the filtration procedure.

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Many radioisotopes that may be included in ground water analyses are isotopes of metals that would be associated with the suspended solids in a water sample. The fact that these elements are radioactive does not influence their chemical behavior. Thus, acidic preservation of the water prior to filtration would result in their desorption from suspended solids.

Volatile organic compounds may be lost in the process of filtration if the water is exposed to the atmosphere or if the filtration occurs with a pressure change across the membrane caused by a vacuum. Most volatile organic compounds listed in the volatile category of the priority pollutants have low to moderate affinity for the solid substrate. Thus, water samples for the volatile analysis are frequently not filtered because the recovery by purging in the presence of suspended matter can be shown to be quantitative. Filtration of water in this context requires a filter placed in the water discharge line. Less desirably, water may be filtered as soon as possible after collection by another means of filtration. As noted, delaying filtration may complicate the acquisition of reliable data if the water has an appreciable iron concentration.

The issue of filtration of ground water is raised

because many timer water collected from memory of weils carries suspended matter as a result of the nature of the sediments or construction of the well. Production wells used for drinking purposes or for other high volume uses are usually constructed to tap a reasonably prolitic aquifer and to produce water with good clarity. In contrast, monitoring wells are sometimes screened in silty or clayey zones and samples may have substantial amounts of fine sediment. The amount of suspended matter is an artifact of the method of water collection and well construction and is not reproducible through time. Anvinfluence the sediment may have on the results of the chemical analysis must be looked on as biasing the sample.

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This discussion is based on the premise that the ground water in question is produced from an unconsolidated aquifer or a crystalline rock aquifer. In some locations where solution-cavitied aquifers are monitored, the aquifer water may be carrying sediment. In the former cases, the assumption is that sediment is not being carried in suspension.

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Opinion II

by Robert M. Burger

Chemical analysis of ground water is becoming increasingly important with the emphasis being placed on its validity and accuracy. Analytical data from ground water samples are being used to determine regulatory compliance, contamination assessment, and waste disposal impacts. The use of this data can also result in a significant financial burden for the site owner if the analysis indicates degradation of the ground water above the regulatory guidelines. For this reason, it has become apparent that field sampling protocol minimize sample degradation or alteration. Analytical data from the laboratory of ground water can only be termed representative and valid if the sampler utilizes the necessary protocols and procedures for monitoring the in situ characteristics at the time of collection. Field filtration is one alteration that can maintain those characteristics and remove man-made interferences caused by the monitoring well installation. Field filtration is performed by forcing the sample through a filter paper, collecting the filtrate and preserving it for the appropriate chemical analysis. The filtrate is usually termed the dissolved or soluble fraction of the ground water. The mean pore diameter of the filter paper has received much discussion (Claassen 1982, Demayo 1978, Gibb 1981) with respect to the appropriate size for ground water samples. The consensus is that a 0.45 micron filter paper will remove the majority of suspended particles while not removing dissolved or colloidal material inherent in ground water. Along with appropriate pore size, discussion has taken place regarding the different types of filtration apparatus and their relative merits (Claassen 1982, Unwin 1982). Pressure filtration with inert gas or in-line filtration without sample contact with the atmosphere appears to be preferred methods. Another method commonly used is with a vacuum source and filter flask; pulling the sample through the filter paper. Regardless of the method or type of equipment, there appears to be general agreement that field filtration is a positive alteration of the sample before chemical analysis.

Field filtration can be viewed as a positive alteration of ground water samples when you consider that most ground water that is moving through soils are of low velocity and thereby not capable of carrying particulate matter. Monitoring wells placed in silts and clays are unusually difficult to develop and upon sample purging can create hydraulic gradients capable of carrying particulate matter into the well. These soil particles, if not removed before preservation and analysis, can produce high concentrations of organic and programic analytes within the sample.

These chemical analytes that are bound to the soil particles that find their way into the monitoring well can and will produce substantial variations within the ground water sample. These variations can be correlated to the level of turbidity or suspended solids within the samples (Strausberg 1983). If the data is being used for regulatory purposes the impact of the sampler's capability of producing turbid-free samples becomes crucial. With the increase in long-term compliance monitoring, the variability of sample collection with different personnel and equipment increases the probability of chemical variations.

Regardless of the type of well installation, sampling procedures, or type of equipment used, samples that are field-filtered should provide a consistent and representative chemical analysis of the ground water.

This viewpoint presents the results of ongoing work to evaluate the effectiveness of field filtration on laboratory analysis of ground water. The data strongly suggests that field filtration be performed at most sites regardless of geology and that field filtration reduces the fluctuations in many of the analysis due to turbidity levels.

Data Collection

Sources

Analytical data is presented and reviewed for 20 monitoring wells from five sites located in northern New England. All of the monitoring wells are currently being used and sampled for assessment of waste disposal impacts or contamination migrating at municipal or industrial waste disposal sites.

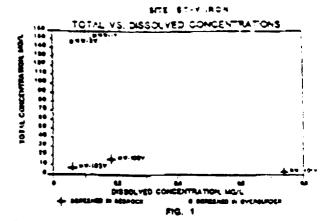
Monitoring wells were chosen at each site for their adequacy of both filtered and unfiltered chemical analysis, along with minimal impacts from waste sources or well construction. The wells are screened in a variety of geologic formations, from marine silts and clays to bedrock. Sample collection, filtration and preservation procedures were reviewed for protocol variations, as well as analytical methodology.

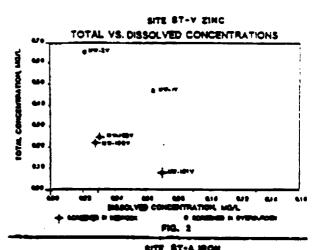
Data Review

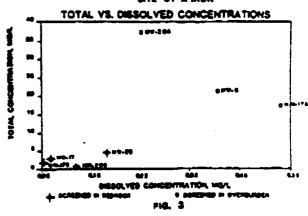
The data presented here is in graphical form. Each graph is a comparison of the average total concentration to the average dissolved concentration for a particular parameter. The samples were initially not filtered and reported as total concentrations over a period of three to five years and subsequent sampling from these same wells had filtration performed over a three- to four-year period. All of the samples were collected by the same personnel using the same equipment and were analyzed by the same laboratory. The analytical precision and accuracy of the methods employed for the analysis were taken into account when assessing the dissolved vs. total concentrations for each parameter.

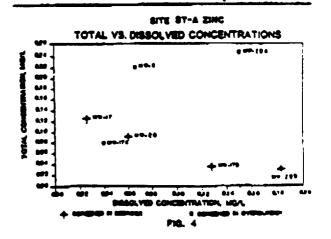
Site ST-V and ST-A

Sites ST-V and A are paper mill sludge disposal landfills and eight monitoring wells are reviewed from both sites. Figure 1 shows the comparison of total vs. dissolved iron at Site ST-V, the older of the two sites. Wells IV and 2V are overburden wells acreened in clays and show a high total iron concentration relative to the dissolved concentration. Wells 100V, 101V, 102V and 103V at the same site are bedrock wells with a correspondingly lower ratio of total to dissolved iron. Figure 2 shows the comparison of total vs. dissolved zinc at site ST-V. Again, wells IV and 2V have the higher ratios of total to dissolved, although a much closer rado than the iron analysis. On both graphs MW-101V have total and dissolved concentrations of iron and zinc that are very similar. An analysis of all the chemical data along with a review of the site hydrogeology indicates that waste









source contamination may be appearing in this well. Figures 3 and 4 show the comparison of total vs. dissolved from and zinc for site ST-A. Wells 6, 17A and 20A are screened in the overburden and again have the higher ratio of total to dissolved concentrations. Wells 17, 17B, 20B and 20 are the bedrock wells and have a lower ratio similar to site ST-V.

It is apparent that the wells in the overburden material have significantly large differences between the total and dissolved state, especially iron. Iron is an especially difficult parameter for assessing filtration effectiveness since other changes in ground water chemistry also affect iron. Oxidation can cause solubie iron to convert to an insoluble form rather quickly (Unwin 1982) and pH and temperature also play an important role in the dissolved concentration of iron. Other metals, although more resistant to oxidation or conversion, can coprecipitate with the insoluble iron. This may cause lower dissolved concentrations of these elements since filtration of the iron precipitates will remove them also.

Site ROC

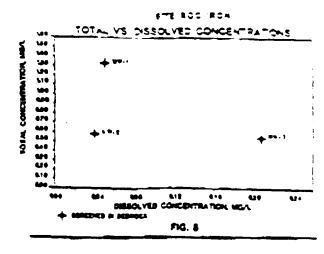
Site ROC is a municipal landfill and three bedrock monitoring wells are compared for total vs. dissolved iron, sulfate and hardness, Figures 5, 6 and 7. As at the previous site, the bedrock wells don't have the dramatic variation between total and dissolved constituents as have the overburden wells. The wells at this site are screened approximately 150 to 250 feet in bedrock. The bedrock is a limestone and as such, flow through this geologic material may be predominantly through solution channels. This is a situation where filtration may not be appropriate for assessment of contaminant migration since the small amounts of suspended solids obtained with the sample may in fact be inherent in the ground water.

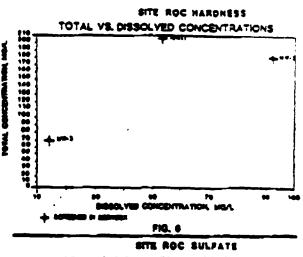
To assess the effect filtration has on the monitoring wells, domestic wells located nearby in the bedrock were compared analytically to the monitoring well data. Approximately 15 domestic wells are sampled on an annual basis and the analysis performed is for total constituents. A comparison of this data with the monitoring well data indicates that the total concentrations of iron, hardness and sulfate in the domestic wells are in relatively close agreement with the dissolved data from the monitoring wells.

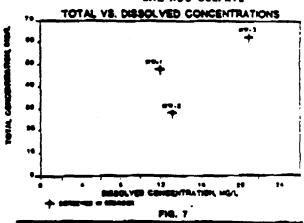
A comparison of the average concentrations from the domestic wells and the monitoring wells are as follows:

Mo	onitoring Wells		Domestic Wells
Parameter	Total	Dissalved	Total
irea	.221	.099	.283
Kardness	146	53	72.4
Sulface	45.33	15.38	22,47

A possible reason for the higher concentrations of total iron, sulfate and hardness in the monitoring wells is the infrequent pumping and possible well installation interferences such as rock particles remaining in fractures.







Site B

Site B is a paper mill sludge disposal site and the three monitoring wells reviewed are used to assess leachate impact on ground water from the sludge and a leachate pond. All three wells are screened within the overburden, mainly clays and silty sands. Figure 3 shows the relationship between total and dissolved iron for the three wells. With the exception of MW-209, the total concentrations are significantly higher. Of the two wells shown in Figure 9 and 10 the dissolved concentrations of magnesium and zine are significantly lower in MW-212 with MW-209 having slightly less of an impact. Both MW-212 and 209 are downgradient

the result of source contamination in the ground water and not a result of the sediment or soil contribution of these two elements. One positive aspect of field filtration is the ability to screen or remove variables during ground water data assessments. Prior to filtration, chemical analysis of MW-209 was erratte and conclusions were not easily drawn on whether source contamination or sediment load were responsible.

Site AU

The last site reviewed is actually a case study or investigation of the causes for highly erratic and variable chemical data from monitoring wells located at a municipal landfill. The client had analytical data from his monitoring wells that was highly variable and had some values above the primary and secondary drinking water standards. An investigation of the analytical data and the field protocols used to collect the samples revealed the following:

- The monitoring wells were not being purged prior to sampling.
- The samples were not field-filtered.
- Samples were prepared for analysis using different protocols as follows:

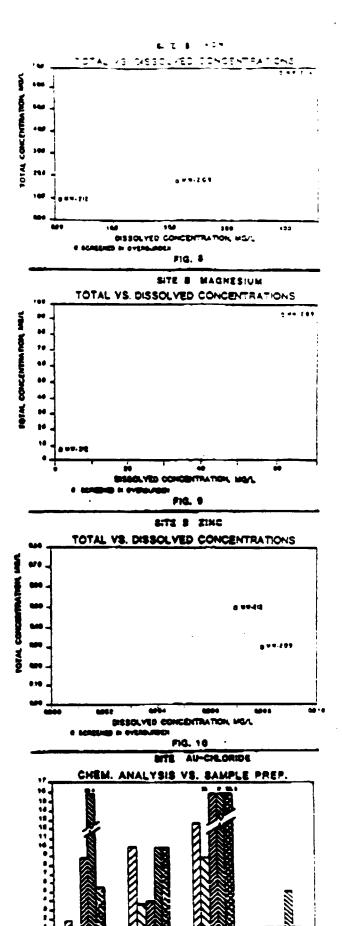
Event 1—Samples were not refrigerated followed by nitric acid addition. The sample was shaken and then filtered through a 0.45 micron filter. The filter was analyzed.

Event 2—Samples were refrigerated and preserved with nitric acid. The sample was shaken and digested followed by filtration through a 0.45 micron filter. The filtrate was analyzed.

Event 3—Samples were refrigerated and preserved with nitric acid. The supernatant was decanted, digested and then filtered through a 0.45 micron filter followed by analysis.

Event 4—Samples were field-filtered, preserved with nitric acid except for chloride and refrigerated. They were then digested and analyzed.

A data comparison was made and found to be significantly different for many of the parameters. Figures 11 though 15 shows a comparison of five parameters for five wells based upon the event and type of field protocol followed. From the graphs it can be seen that field filtration significantly reduced the parameter concentrations on most of the wells. It is obvious that not field-filtering together with digestion of the sediment load created an abnormally high iron content indicative of the soil content rather than of the ground water. Figures 12, 13, 14 and 15 show very similar decreases of copper, iron, lead and zinc much like chloride. Some of the wells that had high turbidity levels also proved to have the largest differences between the total and dissolved concentrations. Again, this situation appears to be typical of wells in low permeability formations and the inherent mineral and therefore chemical constituents of the soil become included in the ground water analytical data when the samples are



Conclusions

Based upon the data collected and reviewed from the 20 monitoring wells the following conclusions have been reached:

- Dissolved concentrations of chemical analytes are significantly lower than the total concentrations for the same well.
- The impact filtration has on chemical concentrations will vary depending upon the geology of the well.
- Monitoring wells are not always installed in geologic material that permits turbid-free water to be collected.
 If chemical analysis from these wells are to be used in contaminant or hydrogeologic assessments, field filtration is required to remove the soil or rock particles not inherent in the ground water.
- Adequate assessment of ground water data having temporal and spatial variations need consistent sampling and analytical protocols performed. Field filtration will provide the same quality filtrate for chemical analysis negating inconsistent sampling protocols.

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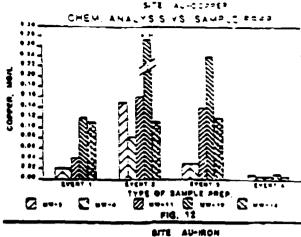
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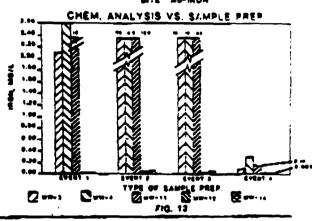
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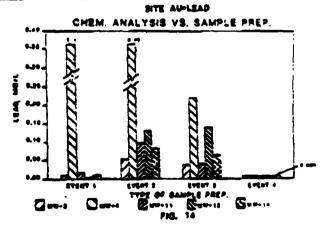
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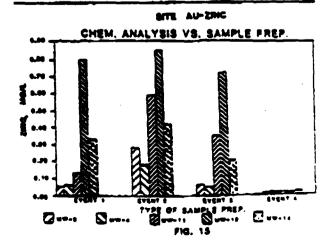
Biographical Sketch

Robert M. Burgar is the monitoring department manager with the E.C. JORDAN CO. in Portland, Maine. He holds on A.A.S. degree in civil technology from SUNY at Dolld. For the past seven years he has coordinated, developed and performed ground water monitoring programs for a variety of hydrogeological investigations for the JORDAN CO. His experience has included hazardous and non-hazardous ground water, vadose zone and general sampling protocol and field analytical technique development. He is a member of the Association of Ground Water Scientists and Engineers, a division of the National Water Well Association.









by John J. Trela. Ph. D.

The objective of any ground water sampling protocol is to obtain a representative sample of ground water.

In practice, this objective is, or should be, controlled by the purpose of the sampling. In selecting a methodology it is critical to have prior knowledge of the context in which the sampling results will be utilized. Will the results be used in a regulatory compliance program for ground water, will they be used to establish background aquifer quality, or will they be used to address potability? In any case, is the ground water in the area used raw (i.e., private, individual wells) or is it treated prior to distribution and use? The answers to these questions are significant since they extend beyond a theoretical view of scientific "accuracy" into the realm of practical significance.

Theoretical Considerations

There is a single key issue to be examined when deciding whether or not to filter a ground water sample before analysis. What are these "things" that are being filtered out and to what extent does their removal affect the ground water quality analysis that is obtained? In this sense, an effect can be either positive or negative, but in either case the sample results do not represent the quality of the ground water as it existed in the aquifer.

Effects such as these that after the "true value" of a parameter in a sample to some "other value" must be recognized and effectively dealt with to achieve the basic purpose and objectives of a sampling program.

Most often, these effects are generated by the process of well sampling itself. They fall into two broad categories—physical and chemical.

Physical effects most often are the result of contamination of the water sample with silt or clay particles from the aquifer matrix. These effects are the product of the sampling process itself (pumping, bailing, etc.), which produce turbulent flow immediately adjacent to the well screen. Turbid ground water samples are obtained from poorly or improperly developed or constructed monitoring wells. Additionally, a turbid sample may be produced from properly constructed and developed wells that are pumped or pursed at rates in excess of their yield. This is especially true if the medicale formation is excessively silty, a condition which characterizes many of our aquifers with marginal yields. It is also a common situation at industrial or landfill sites because of local conditions and/or poorly developed ground water sampling wells. Our sampling objective is to obtain a representative sample of ground water, what we actually obtain is a water sample that is mixed with a sample of the soil or sediment that comprises the aquifer. This presents a significant problem since we know that this soil or sediment is not inert. This will be dealt with subsequently.

Chemical effects are produced when the water sample itself reacts to the change in chemical environment produced by removing the ground water from the aquifer and exposing it to the air. The most graphic example of this type of reaction is the formation of the frequently

observed prange won precipitate or "floo" in the samp e bottle after it is exposed to the air. Depending on curtumstances, significant amounts of flocculation may occur in a matter of a few seconds. In general, most chemical changes are the result of aeration of the sample, which causes radical shifts in dissolved gases such as oxygen or carbon dioxide in the water sample. Such reactions present two basic problems. First, the addition or loss of gases shifts chemical equilibria within the sample. This shift changes the solubility of ionic species in solution and may cause a precipitation reaction to occur. This reaction may directly or indirectly affect the concentration of other dissolved species in the sample which are not reactants involved in forming the precipitate. Simply, precipitates are rarely pure in the chemical sense. This fact is well-recognized by chemists and there is a long string of chemical terms (coprecipitation, solid solution, adsorption, occlusion, postprecipitation), which are employed to describe the various mechanisms that result in the formation of impure precipitates (Flaschka, et al. 1969).

A good example of this problem involves iron and calcium, two elements commonly found in ground water. An acid ground water (pH 5.5) containing calcium (Ca⁻³) and iron (Fe-2) in solution is sampled. The sample is exposed to the air and the iron is exidized ($Fe^{*}-Fe^{*}$) + e). Since ferric iron (Fe') is much less soluble than ferrous iron (Fe⁻²) the ferric iron precipitates as orange ferric hydrous oxide precipitate. The calcium in solution is partially coprecipitated when the iron is precipitated. The amount of calcium in solution is decreased even though under the same conditions, in the absence of iron. all the calcium in solution will remain in solution. Second. with the formation of the precipitate we have a solid in contact with the sample that can react with the liquid to decrease the concentration of other ions in solution by cation or anion exchange, absorption, or postprecipitation reactions. Adsorption of both cations and anions from solution by iron oxides is well-documented in the technical literature. For example, a single review article on iron oxides (Schwertmann and Taylor 1977) identified 13 separate research investigations that showed adsorption of phosphate, molybdate, silicate, sulfate, borate, copper, lead, calcium and zinc ions from solution by iron oxides.

The reaction between the solid and liquid phases in the ground water sample can be pronounced in the case where silt and/or clay particles have been withdrawn from the aquifer with the water. In some cases, depending on the mineralogy of the silt and clay particles these changes can significantly alter the content of species in solution by cation and anion exchange reactions or absorption. The nature and behavior of these reactions are discussed elsewhere (van Olphen 1966, Gast 1977) in greater detail than is possible here.

We cannot assume that the water and the silt come from the same place and must be in equilibrium. To the contrary, we must assume that they are not in equilibrium since we have altered the chemical environment of the water by removing it from the aquifer, exposing it to the

Practical Considerations

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The foregoing theoretical discussion leads to the following practical problem statements. Unfiltered ground water samples are acidified before analysis and substances not in solution can be placed into solution thereby falsely elevating their concentration in the sample. Yet, the filtering of ground water samples can remove substances that were in solution but have precipitated since sampling. thereby falsely depressing their concentration in the sample. At first glance these statements seem to present an insoluble problem. However, there is a solution.

At the first level we should be assured that we are dealing with a legitimate sampling problem and not a problem that is the result of a poorly constructed well. When excessively turbid samples are produced due to a poorly constructed or improperly developed well, the real solution is to rehabilitate or replace the well, not to filter the sample. The technical integrity of the well dictates the technical integrity of the sample. If the well was not properly constructed or developed, why should we assume the well was screened at the proper interval? Filtering is only part of a much larger substantive issue of the value or utility of the well itself. To overcome these problems we have required "as-built" construction certifications for ground water monitoring wells in our ground water regulatory program. In the regulatory program we also specify construction requirements and performance standards for monitoring wells. Monitoring wells are expected to be able to yield at least one to two gallons per minute of turbid-free water. This is done in full recognition of the fast that there are certain geologic circumstances where this performance standard may not be readily attainable. In these cases it is expected that the well drillers' art be practiced at the level necessary to obtain the best results possible. In other cases where the well begins to deliver turbid water after years of use the correct solution is to rehabilitate or replace the well and not to filter the sample. Placing this issue behind us we can effectively deal with those legitimate cases where precipitates or turbidity are real problems.

In certain geologic circumstances where turbidity occurs it can be minimized, and in some cases eliminated, by employing well casing evacuation protocols which minimize turbulent disturbence (low rate peristaktic or bladder pumping, bailing) over those that create excessive turbulence (high-rate centrifugal pumping). However,

them are distinctioned where turne samples are unapplied 20:0

In the practical sense, the uming of filtering is the key consideration in these cases. We have encountered a variety of sampling procedures. Sometimes samples are acidified and then filtered in the field. Sometimes they are field-filtered then acidified. On other occasions samples are acidified and filtered in the laboratory hours to days after they are collected. This variety of procedures reflects the general confusion regarding this issue. In our opinion a superior methodology includes an in-line filtration which is conducted at the time of sampling. In other cases, commonly used procedures which provide for acidification prior to filtering will yield metals analysis which represents the sum of dissolved and exchangeable cations.

The key issues in deciding on acceptable protocols is the context of use of the analytical results. For example, is it realistic to filter samples from ground water monitoring wells in a region where residential use of ground water is from individual wells which are unfiltered and untreated? Clearly not, because the individuals using the aquifer are drinking unfiltered water. Similarly, does it make sense to filter a turbid sample collected from one of the five monitoring wells that are used to determine a facility's compliance under a state discharge permit program or RCRA while not filtering the remaining four wells because they are not turbid?

The simple technical solution to this problem is to split the sample and analyze both a filtered and an unfiltered subsample. Practically, however, these results in : doubling of analytical costs in all cases. In order to reasonably justify the use of split samples, which are analyzed in the filtered and unfiltered states, we mus again place the samples in the appropriate case context

If the purpose of sampling is to assess potability o untreated ground water, two samples can be collected However, only the unfiltered sample needs to be analyze. at the initial stage. If this sample passes drinking water standards or other applicable standards (i.e., state ground water standards), the issue of flitering is moot. Alterna tively, however, if the sample fails the standards, then second analysis on the filtered split may be conducted t determine which portions of the "violation" are attribu table to dissolved and exchangeable fractions. This analsis will lead to a better understanding of the nature ar. distribution of the components in the sample and restric the additional cost to conditions and circumstances whe they are technically justified and necessary.

In cases where precipitates form after the sample collected, the sample should be acidified (pH < 2.6which in almost all cases, will completely redissolve t precipitate. The solution analysis will then correcreflect the original composition of the ground water.

Conclusions

Sample filtration is not the correct solution for de riorated, poorly developed or poorly constructed we that produce turbid samples. Post-sampling precipita should be redissolved by acidification and not filtered.

ine imited number of extimate cases where turbidity is a problem, split samples should be collected and a filtered sample should only be analyzed when there is a regulatory or public health reason to do so. We should not set up simple "yes or no" mechanical procedures to address the filtering of ground water samples. Documentation should be required of the actual procedures used under given circumstances so that analytical results may be properly interpreted. If we oversimplify complex circumstances we will undoubtedly cause numerous errors.

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Biographical Sketch

Dr. John J. Trela is bureau chief for Ground Water Quality Management for the New Jersey Department of Environmental Protection (Division of Water Resources, Bureau of Ground Water Quality Management, CN 029, Trenton, NJ 08625). His responsibilities include administration of New Jersey's integrated ground water quality protection program, which includes the New Jersey ground water discharge permit program, L.U.S.T., U.I.C., and the ground water aspects of RCRA, CERCLA and the New Jersey solid waste programs. Prior to government service, he had provided technical consulting to the private and public sector on soil science, zeohydrolozy, and environmental aspects of land use. Educated at Rutgers University, his specialties include soil science, surficial reology, ground water resources management and forensic environmental science.

Discussion

From the Floor: If you've got a formation with more than 50 percent fines in it, we cannot install a turbid-free well; therefore, can we filter?

Trela: In all cases, no. I would want to look on a case-bycase basis to determine the appropriateness of the
techniques that were used for construction, the type of
pack that was used, whether it was a geotech fabric or
anything else, reasonably based on the type of facility.
And what I mean by that is if you're dealing with a
major hazardous waste facility as opposed to a septic
tank, you might get different answers from me.

From the Floor: So we are still looking at leaving the filter in the ground; is that why we put a sand pack in? Treta: I think there is a generic problem with trying to compensate for the errors that are produced when you bring all these solids into your sample under conditions of changing equilibrium. Short of doing a dissertation on each sample, I don't know how you're going to do that; so I think we really have to depend on the well

that; so I think we really have to depend on the well driller's art and the practical application of solutions to the problem and them only deal with those cases that you have to. And when you have to deal with them, I think, in-line filtration is better. You don't want to have precipitation and exchange reactions and everything else going on simultaneously.

From the Floor: We have gone to low rate pumping—which is -15 gallons per minute.

Trela: It consumes a lot of time though. So there are advantages and disadvantages.

From the Floor: I have two comments. The first one is, I suspect there is a significant difference between vacuum and pressure filtration, one being in-line and quite a bit different in process than pressure filtration. The other comment is that you usually don't have

wells that are consistent in their construction; and often, in order to make the data bases useful, you have to use either on-site wells or wells that were constructed at some previous time with special permission or special construction techniques. The major problem is consistency. You have to use one technique; and my guess would be that the best technique would be in-line pressure filtration.

Burger: That's one of the reasons that we have gone to filtration; only because you have a variety of situations. And to compare apples and apples, old wells, new wells, wells that we really don't have control over, we filter across the board. And obviously, there are problems associated with that, but I don't see how you get around that except on a case-by-case, well-by-well basis. There is a practical side depending on what you're going to use the data for. I think it's important to take a look at what the data is going to be used for and exactly how exact that data needs to be.

Treia: Well, I'll answer the question on consistency from the regulatory perspective. Generically, on well construction in the regulatory programs in New Jersey, we have as-built certifications for monitoring wells. A contractor has got to sign off legally; so that tends to make people a little more careful about what they are telling. We also have construction requirements in regulatory documents. Guidelines on how the wells are to be constructed in addition to performance standards. And again, recognizing that that's not achievable in all cases, but that's what we are shooting for. That is a professional standard we are trying to achieve. In addition to that, we have a certified laboratory program for ground water sample analysis. In other words, anybody just can't analyze a sample and turn it in to a regulatory agency in New Jersey. And we also have licensed well drillers.

We are looking at the concept ngnt now of incorporating all samples. We currently have the requirement that, at least for landfills, the samples must be collected by a certified lab. There are no technical requirements as to qualification, ability, or experience of the people actually collecting ground water samples, and we are looking at that question right now because, as I said, we have seen a lot of people who try to get 50 gallons a minute out of a 2-inch well; and it's obvious after their effice minutes with them, they have no idea what they are trying to do.

m the Floor: How can you rationalize taking ground water samples and comparing your data when you have apsointely no idea of how much solids are in the sample and the solids give you a variability far beyond anything else that you can even conceive? If the shoe were on the other foot and I were the one standing up there telling you that I wanted to sample and keep my solids in it and you were sitting back here as a regulator, you would not allow me to do that because the variability in the samples would be beyond anything that you could see; and yet, you're telling me that that's what you want to do. I can't conceive in my own mind from an analytical point of view how you can get a large variable amount of solids between wells and in the same well even if you sample one right after the other and compare that data.

Trela: I think if that's happening, there are other kinds of problems going on.

From the Floor: I don't care about the level or how much problem there is. What I'm talking about is an analytical technique of comparing your data when you have a variable in there that you're analyzing that you have absolutely no control over and it's representative of what you took out of the well.

Trela: What you're saying, the solution to the variable that's uncontrollable is to filter it out so you don't have to deal with it.

From the Floor: In some cases, it is.

Trela: The point is that people use the concept of filtering the sample as an excuse for bad well construction. That's a very common thing.

From the Floor: I'm not saving that.

Trefs: I wouldn't ask enyone to filter samples or do dual sampling or spend extra money where it wasn't reasonably product to do so. There is a hierarchy of analysis.

From the Floor: We argue about a well casing absorbing miniscule amounts of material, and here we are talking about solids here that are totally variable.

Treis: I think the point that you're not thinking about, at least from my perspective, is that when you get this sample out of the well, you have colloids in it and you have solids. You're drawing a conclusion that everything that's in the solid was in the solid when it was in the ground and that everything that's in the solution was in the solution when it was in ground. I think that's just as incorrect as taking the other perspective and saying dissolve everything and put it in solution. What I have recommended here is that you do the

analysis, do the split sampling where it's necessary

From the Floor. I'll give you your precipitation and oxidation. That goes without saying. That is good chemistry. No problem there. What I'm talking about are colloidal suspensions that are small but you can see them; and I'm talking about the variability from well to well. And if you take the total analysis, particularly on your metals and run them, you're going to get a variability in your data that's going to be irreconcilable no matter what you do.

Trela: It may or may not be, depending upon the formation and how many metals are in there. Let's get rid of a lot of other things.

From the Floor: If you want to know about the soil, I'll give you a soil sample and the analysis; and I won't argue about that.

Trela: What do you do with the water that's in the soil? From the Floor: That's in your water sample.

Trela: That's the reciprocal situation. If I take a core out and it's saturated and I ask for a soil analysis, what do you do with the water?

From the Floor: Either you filter it or you dry it.

Trela: Will I get the same answer whether or not you filter it or dry it?

From the Floor: Maybe not. Trela: Probably not.

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EPA REGION III OA DIRECTIVES

HWMD

Bulletin No. OAD009

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DATE BOOK 3, 1940

FIELD FILTRATION POLICY FOR MONITORING WELL GROUNDWATER SAMPLES REQUIRING METALS ANALYSIS

The objectives of this directive are: (1) to formally state Region III RCRA and CERCLA posity which requires both filterest and unfiltered groundwater samples for metal analyses; (2) to outline appropriate exceptions to the state 1 provide to provide technical direction for the field filtration procedure.

ungle copy of this directive is provided to the individual designated to represent the contractor. It is the responsibility of underlines the directive orthin the contractor organization to appropriate project managers and field personnel.

in the sample. Filtered samples represent dissolved metals concentration and are often more representative of in one contamination (see exceptions below). Monitoring wells sometimes produce turbid water (water containing outspended solids). The turbidity can be due to disruption of the adjacent geologic formations during well purging or poor design and initial development of the well. When particles containing metal species are suspended into the groundwater and are not removed, they dissolve when the sample is preserved to a pH < 2. High levels of manganese, and iron in unfiltered samples often indicate the presence of these particles. Without incontrations of this mobile metal contamination in the groundwater are often over estimated.

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The exceptions to the policy requiring both filtered and unfiltered samples are:

- Site specific geologic conditions where groundwater may transport large particulates and a <u>number of samples are representative of mobile groundwater quality (for example, karst terrain or craw practiculates).</u>
 These site conditions must be fully discussed and documented in the Quality Assurance Proposition QAFJE.
- When there is sufficient historical data (a minimum of four consecutive quarters) from the same monitoring wells that are to be sampled, then these wells may fall into one of the folio ing exception categories:
 - a. If the historical information shows that the purping and sampling methods are the name as the methods to be used at future sampling events, then either likered or unfiltered samples as appropriate to the nationical data are asseptiable for future sampling in these wells.
 - b. If the historical information shows inconsistency between the filtered and unfiltered data, and high revels of aluminum are present in the unfiltered data, only filtered samples are needed.

NOTE: Extrapolation of historical data from a limited number of wells to all the wells at the site is without a clearly justified rationale. All deviations from taking BOTH filtered and unfiltered grounds samples for metals must be fully described and justified in the QAPJP.

Designate an area is which the free environment. When filter Use either a glass or provide an samples.

ction process is to take place. This area must have an element and pustparatus is not in use, keep it covered to protect from authorize particles, apparatus. Stainless steel is unaccipable since it can contaminate the

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Should Ground Water Samples from Monitoring Wells Be Filtered Before Laboratory Analysis?

This is the third of four "Point-Counterpoint" articles planned to appear in this column. These articles are based on discussion sessions held at the Sixth National Aquifer Restoration and Ground Water Monitoring Conference. A one article outlining each speaker's opinion is offered first, followed by the transcript of the discussion session curing which attendees have a chance to ask the speakers questions on the subject.

Opinion I

by Olin C. Braids, Ph.D.

The issue of filtration of ground water samples is integral to discussions of proper protocol in ground reampling. There are those who believe that filtramit to the preparation of a water sample in order to get a legislative and accurate analysis. There are others who are all y convinced that filtration will deletenously affect the water sample and lead to difficulties with the data acquired from it.

Each side of this issue has merit because the reasons for the ground water analysis vary and the objectives in the analytical program also differ. There are legitimate situations in which a ground water sample should not be futered before it is analyzed for its chemical constituents in the laboratory and there are circumstances dictating that an accurate analysis is only obtained when filtration is accomplished. This discussion will address the situations in which filtration should be included in sample preparation.

Filtration in this context is filtration through a 0.45 µm pore-size membrane. The same principles also apply if the filtration medium is glass fiber or paper. Frequently, practical limitations of time and sample characteristics dictate the use of glass fiber or paper as prefilters before the final membrane step.

In dealing with the subject of filtration, one must address the water quality parameters that could be affected either by the act of filtration or by the failure to filter. The following characteristics of water are those that would be affected by filtration or the lack thereof.

The partial pressure of dissolved gases in water withdrawn from the aquifer could be affected by the process of filtration. The relationship of oxygen, carbon dioxide, and perhaps other trace gases influences the pH and the oxidation-reduction potential of the water. In cases where the partial pressure of a gas such as carbon dioxide is significantly affected by the added input from decomposition or some other process, the chemical characteristics of water can change when that retationship is disrupted.

The standard protocol of long standing for dissoived metals is to perform a filtration. Any suspended matter occurring in water is likely to have metal ions adsorbed on it. If the water is preserved with acid prior to analysis as the standard protocols call for, the metals are likely to be desorbed from the solids. This would result in assolved concentrations of metals being higher than any nally existed.

from is frequently found as a constituent of greand water in concentrations, which result in its precipitation when the water is exposed to the oxygen of the atmosphere. Under these conditions the sample of ground water should be filtered as rapidly as possible to prevent contact with the air and to remove any suspended material prior to the addition of acidic preservatives. If the sample contains suspended matter and dissolved iron. addition of the acid prior to filtration may desorb metals. from the suspended matter. If the sample is allowed to be in contact with air for even a matter of minutes prior to filtration, the iron may precipitate and co-precipitate or adsorb metals that were in solution. Acidification of the sample at this point may redissolve the fron but may also bring into solution more of the other metals than were in solution at the time the sample was collected.

The presence of suspender, matter in water, where the water has been in contact with or is contaminated with very slightly soluble organic compounds poses a problem similar to macofishe metals. Slightly soluble compounds such as PC Rs, polynuclear aromatic hydrocarbons, possible reterm, and many pesticides are in this class of an offiltered sample is extracted with organic solvents, malyzed, the compounds will detorp and appear as a cry were in solution.

Radioactive gases such as radon could be affected by filtration because of the pressure change across the filtra-

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Many radioisotopes that may be included in ground water analyses are isotopes of metals that would be associated with the suspended solids in a water sample. The fact that these elements are radioactive does not influence their chemical behavior. Thus, acidic preservation of the water prior to filtration would result in their desorption from suspended solids.

Volatile organic compounds may be lost in the process of filtration if the water is exposed to the atmosphere or if the filtration occurs with a pressure change across the membrane caused by a vacuum. Most volatile organic compounds listed in the volatile category of the priority pollutants have low to moderate affinity for the solid substrate. Thus, water samples for the volatile analysis are frequently not filtered because the recovery by purging in the presence of suspended matter can be shown to be quantitative. Filtration of water in this context requires a filter placed in the water discharge line. Less desirably, water may be filtered as soon as possible after collection by another means of filtration. As noted, delaying filtration may complicate the acquisition of reliable data if the water has an appreciable iron concentration.

The issue of filtration of ground water is raised

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This discussion is based on the premise that the ground water in question is produced from an unconsolidated aquifer or a crystalline rock aquifer. In some locations where solution-cavitied aquifers are monitored, the aquifer water may be carrying sediment. In the former cases, the assumption is that sediment is not being carried in suspension.

Olin C. Braids, Ph.D., is with Geraghty & Miller Inc., Syomet, New York. Tampa Piorida

Opinion II

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by Robert M. Burger

Chemical analysis of ground water is becoming increasingly important with the emphasis being placed on its validity and accuracy. Analytical data from ground water samples are being used to determine regulatory compliance, contamination assessment, and waste disposal impacts. The use of this data can also result in a significant financial burden for the site owner if the analysis indicates degradation of the ground water above the regulatory guidelines. For this reason, it has become apparent that field sampling protocol minimize sample degradation or alteration. Analytical data from the laboratory of ground water can only be termed representative and valid if the sampler utilizes the necessary protocols and procedures for monitoring the in situ characteristics at the time of collection. Field filtration is one alteration that can maintain those characteristics and remove man-made interferences caused by the monitoring well installation. Field filtration is performed by forcing the sample through a filter paper, collecting the filtrate and preserving it for the appropriate themical analysis. The filtrate is usually termed the dissolved or soluble fraction of the ground water. The mean pore diameter of the filter paper has received much discussion (Classen 1982, Demayo 1978, Gibb 1981) with respect to the appropriate size for ground water samples. The consensus is that a 0.45 micron filter paper will remove the majority of suspended particles while not removing dissolved or colloidal material inherent in ground water. Along with appropriate pore size, discussion has taken place regarding the different types of filtration apparatus and their relative merits (Classen 1982, Unwin 1982). Pressure filtration with inert gas or in-line filt in without sample contact with the atmosphere appears be preferred methods. Another method commonly is with a vacuum source and filter flask; pulling the sample through the filter paper. Regardless of the method or type of equipment, there appears to be general agreement that field filtration is a positive alteration of the sample before chemical analysis.

Field filtration can be viewed as a positive alteration of ground water samples when you consider that most ground water that is moving through soils are of low velocity and thereby not capable of carrying particulate matter. Monitoring wells placed in silts and clays are unusually difficult to develop and upon sample purging can create hydraulic gradients capable of carrying particulate matter into the well. These soil particles, if not removed before preservation and analysis, can produce high concentrations of organic and morganic analytes within the sample.

These chemical analytes that are bound to the soil particles that find their way into the monitoring well can and will produce substantial variations within the ground water sample. These variations can be correlated to the level of turbidity or suspended solids within the samples (Strausberg 1983). If the data is being used for regulatory purposes the impact of the sampler's capability of producing turbid-free samples becomes crucial. With the increase in long-term compliance monitoring, the bility of sample collection with different personner equipment increases the probability of chemical varieties.

Regardless of the type of well installation, sampling procedures, or type of equipment used, samples that are field-filtered should provide a consistent and representative chemical analysis of the ground water.

This viewpoint presents the results of ongoing work to evaluate the effectiveness of field filtration on laboratory analysis of ground water. The data strongly suggests that field filtration be performed at most sites regardless of geology and that field filtration reduces the fluctuations in many of the analysis due to turbidity levels.

Data Collection

Sources

Analytical data is presented and reviewed for 20 monitoring wells from five sites located in northern New England. All of the monitoring wells are currently being used and sampled for assessment of waste disposal impacts or contamination migrating at municipal or industrial waste disposal sites.

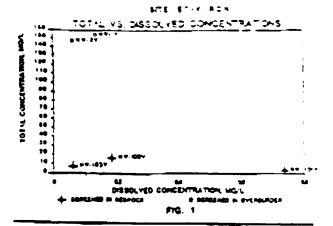
Monitoring wells were chosen at each site for their adequacy of both filtered and unfiltered chemical analysis, along with minimal impacts from waste sources or well construction. The wells are screened in a variety of geologic formations, from marine silts and clays to bedrock. Sample collection, filtration and preservation procedures were reviewed for protocol variations, as well as analytical methodology.

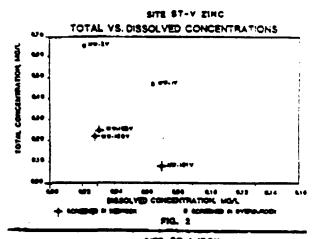
Data Review

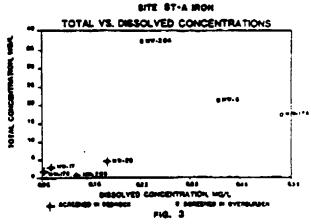
The data presented here is in graphical form. Each graph is a comparison of the average total concentration to the average dissolved concentration for a particular parameter. The samples were initially not filtered and reported as total concentrations over a period of three to five years and subsequent sampling from these same wells had filtration performed over a three- to four-year period. All of the samples were collected by the same personnel using the same equipment and were analyzed by the same laboratory. The analytical precision and accuracy of the methods employed for the analysis were taken into account when assessing the dissolved vs. total concentrations for each parameter.

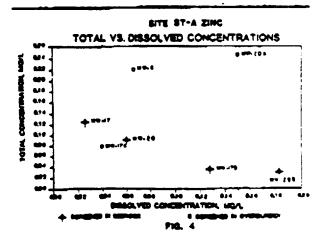
Site ST-V and ST-A

Sites ST-V and A are paper mill sludge disposal landfills and eight monitoring wells are reviewed from both sites. Figure 1 shows the comparison of total vs. dissolved iron at Site ST-V, the older of the two sites. Wells IV and 2V are overburden wells screened in clays and show a high total iron concentration relative to the dissolved concentration. Wells 100V, 101V, 102V and 103V at the same site are bedrock wells with a correspondingly lower ratio of total to dissolved iron. Figure 2 shows the comparison of total vs. dissolved zinc at site ST-V. Again, wells IV and 2V have the higher ratios of total to dissolved, although a much closer ratio than the iron analysis. On both graphs MW-101V have total and dissolved concentrations of iron and zinc that are very similar. An analysis of all the chemical data along with a review of the site hydrogeology indicates that waste









Figures 3 and 4 show the comparison of total vs. dissolved from and zinc for site ST-A. Wells 6, 17A and 20A are screened in the overburden and again have the higher ratio of total to dissolved concentrations. Wells 17, 17B, 20B and 20 are the bedrock wells and have a lower ratio similar to site ST-V.

It is apparent that the wells in the overburden material have significantly large differences between the total and dissolved state, especially iron. Iron is an especially difficult parameter for assessing filtration effectiveness since other changes in ground water chemistry also affect iron. Oxidation can cause solubie iron to convert to an insoluble form rather quickly (Unwin 1982) and pH and temperature also play an important role in the dissolved concentration of iron. Other metals, although more resistant to oxidation or conversion, can coprecipitate with the insoluble iron. This may cause lower dissolved concentrations of these elements since filtration of the iron precipitates will remove them also.

Site ROC

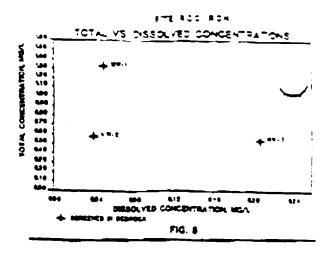
Site ROC is a municipal landfill and three bedrock monitoring wells are compared for total vs. dissolved iron, sulfate and hardness, Figures 5, 6 and 7. As at the previous site, the bedrock wells don't have the dramatic variation between total and dissolved constituents as have the overburden wells. The wells at this site are screened approximately 150 to 250 feet in bedrock. The bedrock is a limestone and as such, flow through this geologic material may be predominantly through solution channels. This is a situation where filtration may not be appropriate for assessment of contaminant migration since the small amounts of suspended solids obtained with the sample may in fact be inherent in the ground water.

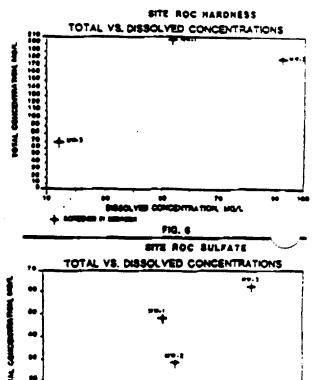
To assess the effect filtration has on the monitoring wells, domestic wells located nearby in the bedrock were compared analytically to the monitoring well data. Approximately 15 domestic wells are sampled on an annual basis and the analysis performed is for total constituents. A comparison of this data with the monitoring well data indicates that the total concentrations of iron, hardness and sulfate in the domestic wells are in relatively close agreement with the dissolved data from the monitoring wells.

A comparison of the average concentrations from the domestic wells and the monitoring wells are as follows:

Average Concentration - mg/L							
	Monitoring Wells		Domestic Wells				
Parameter	Total	Disselved	Total				
lres.	.821	.099	.283				
Hardness	146	53	72.4				
Suiface	45.33	15.38	22_47				

A possible reason for the higher concentrations of total iron, sulfate and hardness in the monitoring wells is the infrequent pumping and possible well installation interferences such as rock particles remaining in fractures.





Site B

Site B is a paper mill studge disposal site and the three monitoring wells reviewed are used to assess leachate impact on ground water from the studge and a leachate pond. All three wells are screened within the overburden, mainly clays and silty sands. Figure 3 shows the relationship between total and dissolved iron for the three wells. With the exception of MW-209, the total concentrations are significantly higher. Of the two wells shown in Figure 9 and 10 the dissolved concentrations of magnesium and zinc are significantly lower in MW-212 with MW-209 having slightly an impact. Both MW-212 and 209 are downgradient

FIG. 7

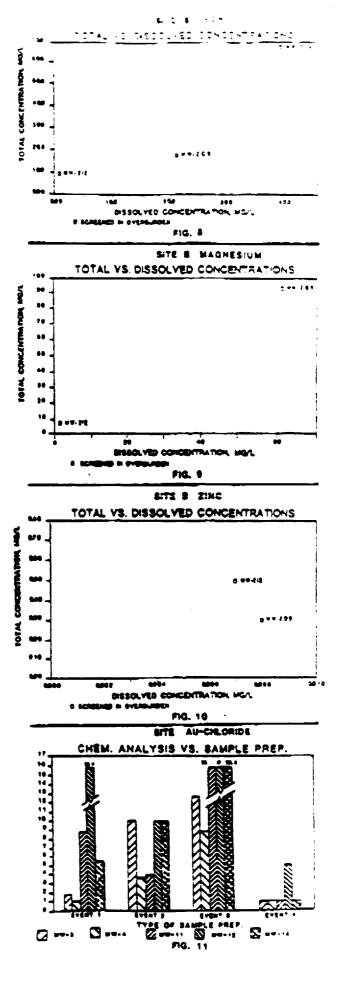
be the result of source contamination in the ground water and not a result of the sediment or soil contribution of these two elements. One positive aspect of field filtration is the ability to screen or remove variables during ground water data assessments. Prior to filtration, chemical analysis of MW-209 was erratic and conclusions were not easily drawn on whether source contamination or sediment load were responsible.

Site AU

The last site reviewed is actually a case study or investigation of the causes for highly erratic and variable chemical data from monitoring wells located at a municipal landfill. The client had analytical data from his monitoring wells that was highly variable and had some values above the primary and secondary drinking water standards. An investigation of the analytical data and the field protocols used to collect the samples revealed the following:

- The monitoring wells were not being purged prior to sampling.
- The samples were not field-filtered.
- Samples were prepared for analysis using different protocols as follows:
- Event 1—Samples were not refrigerated followed by nitric acid addition. The sample was shaken and then filtered through a 0.45 micron filter. The filter was analyzed.
- Event 2—Samples were refrigerated and preserved with nitric acid. The sample was shaken and digested followed by filtration through a 0.45 micron filter. The filtrate was analyzed.
- Event 3—Samples were refrigerated and preserved with nitric acid. The supernatant was decanted, digested and then filtered through a 0.45 micron filter followed by analysis.
- Event 4—Samples were field-filtered, preserved with nitric acid except for chloride and refrigerated. They were then digested and analyzed.

A data comparison was made and found to be significantly different for many of the parameters. Figures 11 though 15 shows a comparison of five parameters for five wells based upon the event and type of field protocol followed. From the graphs it can be seen that field filtration significantly reduced the parameter concentrations on most of the wells. It is obvious that not field-filtering together with digestion of the sediment load created an abnormally high iron content indicative of the soil content rather than of the ground water. Figures 12, 13, 14 and 15 show very similar decreases of copper, iron, lead and zinc much like chloride. Some of the wells that had high turbidity levels also proved to have the largest differences between the total and dissolved concentrations. Again, this situation appears to be typical of wells in low permeability formations and the inherent mineral and therefore chemical constituents of the soil become included in the ground water analytical data when the samples are



Conclusions

Based upon the data collected and reviewed from the 20 monitoring wells the following conclusions have been reached:

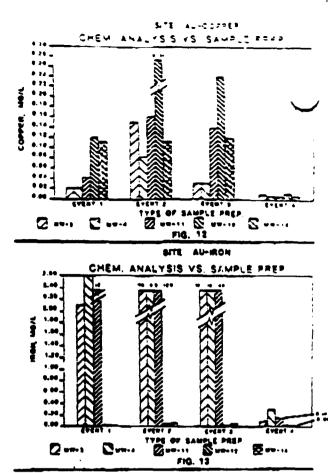
- Dissolved concentrations of chemical analytes are significantly lower than the total concentrations for the same well
- The impact filtration has on chemical concentrations will vary depending upon the geology of the well.
- Monitoring wells are not always installed in geologic material that permits turbid-free water to be collected. If chemical analysis from these wells are to be used in contaminant or hydrogeologic assessments, field filtration is required to remove the soil or rock particles not inherent in the ground water.
- Adequate assessment of ground water data having temporal and spatial variations need consistent sampling and analytical protocols performed. Field filtration will provide the same quality filtrate for chemical analysis negating inconsistent sampling protocols.

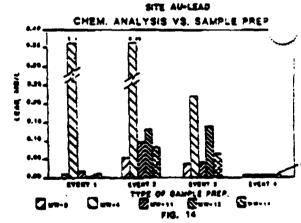
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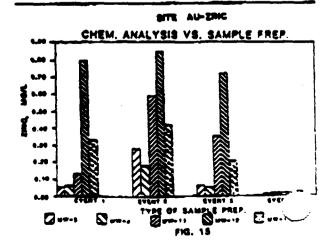
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Biographical Sketch

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by John J. Treia. Ph. D

The objective of any ground water sampling protocol is to obtain a representative sample of ground water.

In practice, this objective is, or should be, controlled by the purpose of the sampling. In selecting a methodology it is critical to have prior knowledge of the context in which the sampling results will be utilized. Will the results be used in a regulatory compliance program for ground water, will they be used to establish background aquifer quality, or will they be used to address potability? In any case, is the ground water in the area used raw (i.e., private, individual wells) or is it treated prior to distribution and use? The answers to these questions are significant since they extend beyond a theoretical view of scientific "accuracy" into the realm of practical significance.

Theoretical Considerations

There is a single key issue to be examined when deciding whether or not to filter a ground water sample before analysis. What are these "things" that are being filtered out and to what extent does their removal affect the ground water quality analysis that is obtained? In this sense, an effect can be either positive or negative, but in either case the sample results do not represent the quality of the ground water as it existed in the aquifer.

Effects such as these that alter the "true value" of a parameter in a sample to some "other value" must be recognized and effectively dealt with to achieve the basic purpose and objectives of a sampling program.

Most often, these effects are generated by the process of well sampling itself. They fall into two broad categories—physical and chemical.

Physical effects most often are the result of contamination of the water sample with silt or clay particles from the aquifer matrix. These effects are the product of the sampling process itself (pumping, bailing, etc.), which produce turbulent flow immediately adjacent to the well screen. Turbid ground water samples are obtained from poorly or improperly developed or constructed monitoring wells. Additionally, a turbid sample may be produced from properly constructed and developed wells that are pumped or purged at rates in excess of their yield. This is especially true if the mologic formation is excessively silty, a condition which characterizes many of our aquifers with marginal yields. It is also a common situation at industrial or landfill sites because of local conditions and/or poorly developed ground water sampling wells. Our sampling objective is to obtain a representative sample of ground water, what we actually obtain is a water sample that is mixed with a sample of the soil or sediment that comprises the aquifer. This presents a significant problem since we know that this soil or sediment is not inert. This will be dealt with subsequently.

Chemical effects are produced when the water sample itself reacts to the change in chemical environment produced by removing the ground water from the aquifer and exposing it to the air. The most graphic example of this type of reaction is the formation of the frequently

Posemino prange won precipitate or Tilloci us ine tamb n bottle after it is exposed to the air. Depending on problemstances, significant amounts of flocculation may occur in a matter of a few seconds. In general, most chemical changes are the result of aeration of the sample, which causes radical shifts in dissolved gases such as oxygen or carbon dioxide in the water sample. Such reactions present two basic problems. First, the addition or loss of gases shifts chemical equilibria within the sample. This shift changes the solubility of ionic species in solution and may cause a precipitation reaction to occur. This reaction may directly or indirectly affect the concentration of other dissolved species in the sample which are not reactants involved in forming the precipitate. Simply, precipitates are rarely pure in the chemical sense. This fact is well-recognized by chemists and there is a long string of chemical terms (coprecipitation, solid solution, adsorption, occlusion, postprecipitation), which are employed to describe the various mechanisms that result in the formation of impure precipitates (Flaschka, et al.

A good example of this problem involves iron and calcium, two elements commonly found in ground water. An acid ground water (pH 5.5) containing calcium (Ca-2) and iron (Fe²) in solution is sampled. The sample is exposed to the air and the iron is oxidized (Fe'-Fe') + e). Since ferric iron (Fe⁻¹) is much less soluble than ferrous iron (Fe-2) the ferric iron precipitates as orange ferric hydrous oxide precipitate. The calcium in solution is partially coprecipitated when the iron is precipitated. The amount of calcium in solution is decreased even though under the same conditions, in the absence of iron. all the calcium in solution will remain in solution. Second. with the formation of the precipitate we have a solid in contact with the sample that can react with the liquid to decrease the concentration of other ions in solution by cation or anion exchange, absorption, or postprecipitation reactions. Adsorption of both cations and anions from solution by iron oxides is well-documented in the technical literature. For example, a single review article on iron oxides (Schwertmann and Taylor 1977) identified 13 separate research investigations that showed adsorption of phosphate, molybdate, silicate, sulfate, borate, copper, lead, calcium and zinc ions from solution by tron oxides.

The reaction between the solid and liquid phases in the ground water sample can be pronounced in the case where silt and/or clay particles have been withdrawn from the aquifer with the water. In some cases, depending on the mineralogy of the silt and clay particles these changes can significantly alter the content of species in solution by cation and anion exchange reactions or absorption. The nature and behavior of these reactions are discussed elsewhere (van Olphen 1966, Gast 1977) in greater detail than is possible here.

We cannot assume that the water and the silt come from the same place and must be in equilibrium. To the contrary, we must assume that they are not in equilibrium since we have altered the chemical environment of the water by removing it from the aquifer, exposing it to the

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The maction between soud phases greenpitates or clay in suspension) and the solution phase (ground water sample) can be profound. The reactions between the solid and liquid phases in natural systems (soils, ground waters) are largely defined by redox reactions and pH as they affect solubility and exchange reactions. The interrelationships, although exceedingly complex, are dealt with in a quite elegant manner in the work of Lindsay (1979). However, even this work has significant limitations since it deals with a limited number of ionic species and does not simultaneously address the number of chemical species commonly found in ground water and their synergisms or antagonisms.

Practical Considerations

The foregoing theoretical discussion leads to the following practical problem statements. Unfiltered ground water samples are acidified before analysis and substances not in solution can be placed into solution thereby falsely elevating their concentration in the sample. Yet, the filtering of ground water samples can remove substances that were in solution but have precipitated since sampling, thereby falsely depressing their concentration in the sample. At first glance these statements seem to present an insoluble problem. However, there is a solution.

At the first level we should be assured that we are dealing with a legitimate sampling problem and not a problem that is the result of a poorly constructed well. When excessively turbid samples are produced due to a poorly constructed or improperly developed well, the real solution is to rehabilitate or replace the well, not to filter the sample. The technical integrity of the well dictates the technical integrity of the sample. If the well was not properly constructed or developed, why should we assume the well was screened at the proper interval? Filtering is only part of a much larger substantive issue of the value or utility of the well itself. To overcome these problems we have required "as-built" construction certifications for ground water monitoring wells in our ground water regulatory program. In the regulatory program we also specify construction requirements and performance standards for monitoring wells. Monitoring wells are expected to be able to yield at least one to two gallons per minute of turbid-free water. This is done in full recognition of the fact that these are certain geologic circumstances where this performance standard may not be readily attainable. In those cases it is expected that the well drillers' art be practiced at the level necessary to obtain the best results possible. In other cases where the well begins to deliver turbid water after years of use the correct solution is to rehabilitate or replace the well and not to filter the sample. Placing this issue behind us we can effectively deal with those jegitimate cases where precipitates or turbidity are real problems.

In certain geologic circumstances where turbidity occurs it can be minimized, and in some cases eliminated, by employing well casing evacuation protocols which minimize turbulent disturbance (low rate peristakic or bladder pumping, bailing) over those that create excessive turbulence (high-rate centrifugal pumping). However,

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in the practical sense, the timing of filtering is the ker consideration in these cases. We have encountered ; variety of sampling procedures. Sometimes same or an acidified and then filtered in the field. Sometime, field-filtered then acidified. On other occasions ? are acidified and filtered in the laboratory hours to ay after they are collected. This variety of procedures reflect the general confusion regarding this issue. In our opinio a superior methodology includes an in-line filtratio which is conducted at the time of sampling. In othe cases, commonly used procedures which provide fo acidification prior to filtering will yield metals analy which represents the sum of dissolved and exchangeac.

The key issues in deciding on acceptable protocols the context of use of the analytical results. For example is it realistic to filter samples from ground water monito ing wells in a region where residential use of groun water is from individual wells which are unfiltered an untreated? Clearly not, because the individuals using the aquifer are drinking unfiltered water. Similarly, does make sense to filter a turbid sample collected from one a the five monitoring wells that are used to determine facility's compliance under a state discharge permit pro gram or RCRA while not filtering the remaining for wells because they are not turbid?

The simple technical solution to this problem is t split the sample and analyze both a filtered and an unfi tered subsample. Practically, however, these results in doubling of analytical costs in all cases. In reasonably justify the use of split samples, w analyzed in the filtered and unfiltered states, we are again place the samples in the appropriate case contex

If the purpose of sampling is to assess potability untreated ground water, two samples can be collecte However, only the unfiltered sample needs to be analyze at the initial stage. If this sample passes drinking wat standards or other applicable standards (i.e., state grout water standards), the issue of flitering is moot. Altern tively, however, if the sample fails the standards, then second analysis on the filtered split may be conducted determine which portions of the "violation" are attrib table to dissolved and exchangeable fractions. This ana sis will lead to a better understanding of the nature a distribution of the components in the sample and restrict the additional cost to conditions and circumstances who they are technically justified and necessary.

In cases where precipitates form after the sample collected, the sample should be acidified (pH ≤ 2 . which in almost all cases, will completely redissolve precipitate. The solution analysis will then correct reflect the original composition of the ground water.

Conclusions

Sample filtration is not the correct solution for de riorated, poorly developed or poorly constructed w that produce turbid samples. Post-sampling should be redissolved by acidification and notice

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o the **Linu** f the o the a problem, split samples should be collected and a filtered sample should only be analyzed when there is a regulatory or public health reason to do so. We should not set up simple "yes or no" mechanical procedures to address the filtering of ground water samples. Documentation should be required of the actual procedures used under given circumstances so that analytical results may be properly interpreted. If we oversimplify complex circumstances we will undoubtedly cause numerous errors.

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Biographical Sketch

Dr. John J. Trela is bureau chief for Ground Water Quality Management for the New Jersey Department of Environmental Protestion (Division of Water Resources. Bureau of Ground Water Quality Management, CN 029 Trenton, NJ 08625). His responsibilities include administration of New Jersey's integrated ground water quality protection program, which includes the New Jersey ground water discharge permit program, L.U.S.T., U.I.C., and the ground water aspects of RCRA, CERCLA and the New Jersey solid waste programs. Prior to government service, he had provided technical consulting to the private and public sector on soil science, zeohydrology, and environmental aspects of land use. Educated at Rutgers University, his specialties include soil science, surficial reology, ground water resources management and forensic environmental science.

Discussion

From the Floor: If you've got a formation with more than 50 percent fines in it, we cannot install a turbid-free well; therefore, can we filter?

Trels: In all cases, no. I would want to look on a case-bycase basis to determine the appropriateness of the techniques that were used for construction, the type of pack that was used, whether it was a geotech fabric or anything else, reasonably based on the type of facility. And what I mean by that is if you're dealing with a major hazardous waste facility as opposed to a septic tank, you might get different answers from me.

From the Floor: So we are still looking at leaving the filter in the ground; is that why we put a sand pack in?

Trela: I think there is a generic problem with trying to

compensate for the errors that are produced when you bring all these solids into your sample under conditions of changing equilibrium. Short of doing a dissertation on each sample, I don't know how you're going to do that; so I think we really have to depend on the well driller's art and the practical application of solutions to the problem and then only deal with those cases that you have to. And when you have to deal with them, I think, in-line filtration is better. You don't want to have precipitation and exchange reactions and everything else going on simultaneously.

From the Floor: We have gone to low rate pumping—which is -15 gallons per minute.

Treia: It consumes a lot of time though. So there are advantages and disadvantages.

From the Floor: I have two comments. The first one is, I suspect there is a significant difference between vacuum and pressure filtration, one being in-line and quite a bit different in process than pressure filtration. The other comment is that you usually don't have

wells that are consistent in their construction; and often, in order to make the data bases useful, you have to use either on-site wells or wells that were constructed at some previous time with special permission or special construction techniques. The major problem is consistency. You have to use one technique; and my guess would be that the best technique would be in-line pressure filtration.

Burger: That's one of the reasons that we have gone to filtration; only because you have a variety of situations. And to compare apples and apples, old wells, new wells, wells that we really don't have control over, we filter across the board. And obviously, there are problems associated with that, but I don't see how you get around that except on a case-by-case, well-by-well basis. There is a practical side depending on what you're going to use the data for. I think it's important to take a look at what the data is going to be used for and exactly how exact that data needs to be.

Trela: Well, I'll answer the question on consistency from the regulatory perspective. Generically, on well construction in the regulatory programs in New Jersey, we have as-built certifications for monitoring wells. A contractor has got to sign off legally; so that tends to make people a little more careful about what they are telling. We also have construction requirements in regulatory documents. Guidelines on how the wells are to be constructed in addition to performance standards. And again, recognizing that that's not achievable in all cases, but that's what we are shooting for. That is a professional standard we are trying to achieve. In addition to that, we have a certified laboratory program for ground water sample analysis. In other words, anybody just can't analyze a sample and turn it in to a regulatory agency in New Jersey. And we also have licensed well drillers.

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We are looking at the concept right now of incorporating all samples. We currently have the requirement that, at least for landfills, the samples must be collected by a certified lab. There are no technical requirements as to qualification, ability, or experience of the people actually collecting ground water samples, and we are looking at that question right now because, as I said, we have seen a lot of people who try to get 50 gallons a minute out of a 2-inch well; and it's obvious after a life there five minutes with them, they have no idea that they are trying to do.

in the Floor: How can you rationalize taking ground water ramples and comparing your data when you have apsolutely no idea of how much solids are in the sample and the solids give you a variability far beyond anything else that you can even conceive? If the shoe were on the other foot and I were the one standing up there telling you that I wanted to sample and keep my solids in it and you were sitting back here as a regulator, you would not allow me to do that because the variability in the samples would be beyond anything that you could see; and yet, you're telling me that that's what you want to do. I can't conceive in my own mind from an analytical point of view how you can get a large variable amount of solids between wells and in the same well even if you sample one right after the other and compare that data.

Trela: I think if that's happening, there are other kinds of problems going on.

From the Floor: I don't care about the level or how much problem there is. What I'm talking about is an analytical technique of comparing your data when you have a variable in there that you're analyzing that you have absolutely no control over and it's representative of what you took out of the well.

Treia: What you're saying, the solution to the variable that's uncontrollable is to filter it out so you don't have to deal with it.

From the Floor: In some cases, it is.

Trels: The point is that people use the concept of filtering the sample as an excuse for bad well construction. That's a very common thing.

From the Floor: I'm not saying that.

Trefa: I wouldn't ask anyone to filter samples or do dual sampling or spend extra money where it wasn't reasonably prudent to do so. There is a hierarchy of analysis.

From the Floor: We argue about a well casing absorbing miniscule amounts of material, and here we are talking about solids here that are totally variable.

Treis: I think the point that you're not thinking about, at least from my perspective, is that when you get this sample out of the well, you have colloids in it and you have solids. You're drawing a conclusion that everything that's in the solid was in the solid when it was in the ground and that everything that's in the solution was in the solution when it was in ground. I think that's just as incorrect as taking the other perspective and saying dissolve everything and put it in solution. What I have recommended here is that you do the

From the Floor: I'll give you your precipitation and oxidation. That goes without saying. That is good chemistry. No problem there. What I'm talking about are colloidal suspensions that are small but yo see them; and I'm talking about the variability well to well. And if you take the total analysis, particularly on your metals and run them, you're going to get a variability in your data that's going to be irreconcilable no matter what you do.

Trela: It may or may not be, depending upon the formation and how many metals are in there. Let's get rid of a lot of other things.

From the Floor: If you want to know about the soil. [7] give you a soil sample and the analysis, and I won't argue about that.

Trels: What do you do with the water that's in the soil? From the Floor: That's in your water sample.

Treta: That's the reciprocal situation. If I take a core out and it's saturated and I ask for a soil analysis, *nat do you do with the water?

From the Floor: Either you filter it or you dry it.

Trela: Will I get the same answer whether or not you filter

From the Floor: Maybe not. Treia: Probably not.

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EPA REGION III OA DIRECTIVES

HWMD

Bulletin No. OAD009

Date April 3, 140

FIELD FILTRATION POLICY FOR MONITORING WELL GROUNDWATER SAMPLES REQUIRING METALS ANALYSIS

The objectives of this directive are: (1) to formally state Region III RCRA and CERCLA policy which requires both filtered and unfiltered groundwater samples for metal analyses; (2) to outline appropriate exceptions to the state 17-10-10 and (3) to provide technical direction for the field filtration procedure.

ungle copy of this directive is provided to the individual designated to represent the contractor. It is the responsibility of unfaithful the directive within the contractor organization to appropriate project managers and field personner.

increasion in as of metal contaminants measured in unfiltered groundwater represent the total metals prese. In the sample. Filtered samples represent dissolved metals concentration and are often more representative of in the communication (see exceptions below). Monitoring wells sometimes produce turbid water (water containing inspended solids). The turbidity can be due to disruption of the adjacent geologic formations during well purping or poor design and initial development of the well. When particles containing metal species are suspended into the groundwater and are not removed, they dissolve when the sample is preserved to a pH <2. High levels of manganese, and iron in unfiltered samples often indicate the presence of these particles. Without incentrations of this mobile metal contamination in the groundwater are often over estimated.

The containing to take both filtered and unfiltered samples to fully characterize the distribution of metals between particulate and distribution preservation for dissolved metals samples must be performed after filtration. Because the containing south filtration must occur immediately after sampling.

The exceptions to the policy requiring both filtered and unfiltered samples are:

- Site specific geologic conditions where groundwater may transport large particulates and the house of samples are representative of mobile groundwater quality (for example, karst terrain or endular passes caucies).

 These site conditions must be fully discussed and documented in the Quality Assurance Project is that tOAFJE.
- 2. When there is sufficient historical data (a minimum of four consecutive quarters) from the same monitoring wells that are to be sampled, then these wells may fall into one of the folio-ing exception categories:
 - 2. If the historical information shows that the purping and sampling methods are the same as the methods to be used at future sampling events, then either likered or unfiltered samples as appropriate to the autorical data are comptable for future sampling in these wells.
 - b. If the bisterical information shows inconsistency between the filtered and unfiltered data, and high levels of aluminum are present in the unfiltered data, only filtered samples are needed.

NOTE: Extrapolation of historical data from a limited number of wells to all the wells at the site is a without a clearly justified rationale. All deviations from taking BOTH filtered and unfiltered grounds samples for metals must be fully described and justified in the QAPJP.

TECHNICAL GUIDANCE FOR FILE RATION OF MONITORING WELL SAMPLES FOR METALS . . . LASIS

Designate an area in which the free environment. When filter Use either a glass or processing samples.

tion process is to take place. This area must have an element and quateparatus is not in use, keep it covered to protect from unborne particles. apparatus. Stainless steel is unacci, able since it can contaminate the

(over)